

The Electronic Contribution to the Elastic Properties of Germanium

Abstract: Theories of several elastic effects resulting from the contribution of electrons to the strain energy function of germanium are presented. They show that the elastic properties are appreciably changed by doping with donor and acceptor impurities. The properties considered are: (1) volume, (2) elastic constants of degenerate *n*-type material, (3) third-order elastic constants of degenerate *n*-type material, (4) elastic constants of degenerate *p*-type material, (5) elastic constants of material containing electrons bound to donors, (6) elastic constants of material containing electrons bound to pairs of donor atoms. The most striking effect is found for the case of degenerate *n*-type germanium, in which the theory predicts that c_{44} can be lowered by 8% with attainable doping levels.

1. Introduction

Piezoresistance experiments show that the electronic energy levels of a multivalley semiconductor depend on the state of strain of the semiconductor crystal.¹ The dependence of the electronic energy levels on strain implies that the strain energy function of the crystal will depend on the occupation of the electronic levels. The purpose of this paper is to evaluate the effect of the electronic part of the strain energy on the elastic properties of germanium. Several of the effects which we predict here should be experimentally observable.

Electronic effects are very important in metals. Jones and co-workers² have attempted to interpret some features of the elastic properties of metals in terms of multivalley-type models similar to those used here. A quantitative interpretation of the effects in metals is not possible at present, however, because of the lack of information concerning parameters of the models such as deformation potential constants, effective masses, and carrier concentrations. Such parameters are accurately known for germanium, which therefore offers a unique opportunity for the study of the influence of the electronic energy on the elastic constants.

Impure germanium can be divided into two classes: (1) If there are more than about 2×10^{17} electrically active impurities per cm^3 the electrons remain in the conduction band at all temperatures. They therefore form a degenerate electron gas at very low temperature. This kind of germanium is called *degenerate germanium*. (2) If there are less than 10^{17} impurities per cm^3 the electrons are trapped in localized states associated with

the impurity atoms at low temperatures. These localized states have energies just beyond the edge of the relevant band and are derived from and have properties closely related to the states of that band. The two cases are described by different models and will be treated separately here.

The values of various parameters of germanium which will be needed in the subsequent calculations are given in Table 1.

2. Model of the conduction band

The model of the conduction band used here is the multivalley model as described by Herring.³ The energy surface has four minima, one on each of the (111) type axes at the Brillouin zone boundary. The states in the conduction band which are occupied by electrons have energies near the minimum energy and crystal momentum vectors $\mathbf{p}$ grouped around the position of the minima in $\mathbf{p}$ space. The states near minimum (*i*) are said to constitute "valley" (*i*).

The valleys can be transformed into one another by the crystal symmetry transformations in an unstrained germanium crystal. Therefore any scalar property must have the same value for all valleys. Any second-rank tensor property must differ only in the orientation of the tensor for different valleys. Further, since the (111) axes are axes of three-fold symmetry, a second-rank tensor property of valley (*i*) must be invariant under a rotation ($2\pi/3$) about the (111) axis which locates valley (*i*).

Thus it must have the form

$$\mathbf{M}^{(i)} = \begin{vmatrix} M_x & 0 & 0 \\ 0 & M_x & 0 \\ 0 & 0 & M_z \end{vmatrix}, \quad (2.1a)$$

where coordinate z is the coordinate along the axis of valley (i). Let $\mathbf{a}^{(i)}$ be a unit vector along the (111) axis of valley (i). Then Eq. (2.1a) can be written in the form

$$\mathbf{M}^{(i)} = M_x \mathbf{1} + (M_z - M_x) \mathbf{a}^{(i)} \mathbf{a}^{(i)}. \quad (2.1b)$$

Here $\mathbf{1}$ is the identity tensor.

The effect of elastic strain on the band structure can be described by the deformation potential approximation. Strain changes the band structure only by changing the energy of all states of a particular valley by the same amount in the deformation potential approximation. The effect of strain on valley (i) can therefore be described by the change of $E^{(i)}$, the energy of the state of lowest energy in valley (i). The most general linear dependence of $E^{(i)}$ on the strain tensor ϵ has the form

$$E^{(i)} = \Xi^{(i)} : \epsilon. \quad (2.2)$$

Here $E^{(i)}$ is measured from its value in the unstrained crystal as zero of energy. ϵ is the strain tensor and $\Xi^{(i)}$ is a second-rank tensor called the *deformation potential constant tensor*. The components of $\Xi^{(i)}$ are called *deformation potential constants*. $\Xi^{(i)}$ must have the form of Eq. (2.1b). It is customary to define $\Xi_d \equiv \Xi_x$ and $\Xi_u \equiv \Xi_z - \Xi_x$ and to write

$$\Xi^{(i)} = \Xi_d \mathbf{1} + \Xi_u \mathbf{a}^{(i)} \mathbf{a}^{(i)}. \quad (2.3)$$

Table 1 Properties of germanium

Property	Value
Elastic Constant	
$B = (1/3)(c_{11} + 2c_{12})$	0.76×10^{12} dynes/cm ²
c_{44}	0.68
$C' = (1/2)(c_{11} - c_{12})$	0.415
Conduction Band	
$m^* = (m_v^* m_l)^{1/3}$	0.22 m_0
Ξ_u	19 eV ^{a, b, c}
Ξ_d	-8 eV ^{a, b}
Valence Band	
m_v^*	0.3 m_0
Ξ_s'	5 eV ^{a, d}
Ξ_d'	-2 eV ^a

^a See Reference 1 for discussion and references.

^b C. Herring and E. Vogt, *Phys. Rev.* **101**, 944 (1956); W. Dumke, *Phys. Rev.* **101**, 531 (1956); C. Herring, T. H. Geballe and J. E. Kunzler, *Bell System Tech. J.* **38**, 657 (1959).

^c See Reference 8.

^d W. H. Kleiner and L. M. Roth, *Phys. Rev. Letters* **2**, 334 (1959).

3. Volume

The contribution of the effect of dilatational strain on the electronic energy to the total energy of the crystal will be examined in this section. Dilatational strain does not destroy the crystal symmetry. The $E^{(i)}$ are therefore all the same. The effect of dilatational strain on the energy of an electronic state is the same for the states of the conduction band and for the bound donor states. Therefore, the considerations of this section are applicable to both of the classes of germanium described in Section 1. The electronic energy in the presence of a dilatational strain is:

$$W_e = NE^{(i)}, \quad (3.1)$$

where N is the electron concentration and $E^{(i)}$ is given by Eq. (2.2). The strain tensor has the form

$$\epsilon = \mathbf{1}(\delta c/c) \quad (3.2)$$

where c is the lattice constant. It can be seen from Eqs. (2.3) and (3.2) that for all (i),

$$E^{(i)} = (3\Xi_d + \Xi_u)(\delta c/c).$$

The total energy of dilatation is the sum of an elastic part, W_g , and the electronic part:

$$W = (9/2)B(\delta c/c)^2 + N(3\Xi_d + \Xi_u)(\delta c/c).$$

Here B is the bulk modulus and is related to the ordinary elastic constants by $B = (c_{11} + 2c_{12})/3$. Minimizing the energy with respect to $(\delta c/c)$ shows that the electronic effect changes the lattice parameter by an amount

$$(\delta c/c) = -N(3\Xi_d + \Xi_u)/9B. \quad (3.3)$$

Values of $(3\Xi_d + \Xi_u)$ derived from experiment contain considerable experimental uncertainty. It appears, however, that $(3\Xi_d + \Xi_u)$ lies between -4 eV and -8 eV. We have chosen the value -6 eV for use in the calculations of this section and have entered this value in Table 1. Thus

$$(\delta c/c) = +1.4 \times 10^{-24} N,$$

where N is the concentration of donors in cm⁻³. The solubility of donor impurities limits the maximum value of N which can be attained to about 5×10^{19} cm⁻³. Thus the maximum value of $(\delta c/c)$ is about $+7 \times 10^{-5}$, a barely observable effect.

A similar calculation can be carried out for p -type germanium. The quantity $3\Xi_d'$, which corresponds to $(3\Xi_d + \Xi_u)$ for p -Ge, has a value of about -6 eV. The energy of the unoccupied electronic states in the valence band must be subtracted from the energy of the intrinsic crystal, so that the effect is again an expansion of the lattice. Its magnitude is roughly

$$(\delta c/c) = +1.4 \times 10^{-24} N.$$

Acceptor impurities are more soluble than donors. A solubility of 5×10^{20} cm⁻³ has been reported for gallium. Thus the maximum effect for p -Ge is $(\delta c/c) \approx 10^{-3}$, which should be easily observable.

4. Shear elastic constants of degenerate *n*-type Ge

The application of a pure shear strain to *n*-type germanium does not change the total electronic energy to terms of first order in the strain. The energy may be changed in terms of second order in the strain, however. This dependence of the energy on terms of second order in the strain amounts to a change in the elastic constants, which will be calculated in this section for the degenerate case, in which the electrons remain in the conduction band at all temperatures.

The density of electronic states of valley (*i*) is

$$N^{(i)}(E) = \frac{4\pi}{h^3} (2m^*)^{3/2} (E - E^{(i)})^{1/2}. \quad (4.1)$$

Here m^* is the density of states effective mass of a valley and $E^{(i)}$ is the minimum energy of valley (*i*). (m^* is related to the transverse effective mass m_t and the longitudinal effective mass m_l by $m^* = (m_t^2 m_l)^{1/3}$). A parabolic band has been assumed. $n^{(i)}$, the concentration of electrons in valley (*i*), is determined by the Fermi level. It is

$$n^{(i)} = \int_{E^{(i)}}^{\infty} N^{(i)}(E) f_0(E) dE \\ = 2\pi^{-1/2} N_c F_{1/2}(\eta - w^{(i)}). \quad (4.2)$$

Here the following notation has been introduced:

$$f_0 = [1 + \exp(E - \zeta/kT)]^{-1} \quad (4.3)$$

$$\zeta = \text{Fermi energy} \quad (4.4)$$

$$\eta = \zeta/kT \quad (4.5)$$

$$w^{(i)} = E^{(i)}/kT \quad (4.6)$$

$$N_c = 2(2\pi m^* kT/h^2)^{3/2}. \quad (4.7)$$

$F_{1/2}$ is the Fermi integral as usually defined.⁴ ζ is determined by the condition that the $n^{(i)}$ must add up to the total concentration of electrons

$$N = \sum n^{(i)}. \quad (4.8)$$

Σ as used here means summation over the four valleys.

The total free energy per unit volume of the electrons in valley (*i*) is

$$A^{(i)} = n^{(i)} \zeta + kT \int_{E^{(i)}}^{\infty} N^{(i)}(E) \log f_0(E) dE \\ = 2\pi^{-1/2} N_c kT [\eta F_{1/2}(\eta - w^{(i)}) - \frac{2}{3} F_{3/2}(\eta - w^{(i)})]. \quad (4.9)$$

In this section the $w^{(i)}$ will be regarded as arising from the strain according to Eqs. (2.2) and (4.6). The strain also changes the Fermi level, ζ . The change in ζ is determined by Eq. (4.8). From Eqs. (4.2) and (4.8)

$$N = 2\pi^{-1/2} N_c \Sigma F_{1/2}(\eta - w^{(i)}).$$

The elastic constants are calculated by considering infinitesimal strains and expanding the strain-dependent

parts of the Fermi integrals in terms of quantities proportional to the strain. To this end it is convenient to write η as

$$\eta = \eta_0 + \delta,$$

where η_0 is (ζ/kT) in the unstrained lattice and δ is the change of η with strain. Thus

$$N = 2\pi^{-1/2} N_c \Sigma [F_{1/2}(\eta_0) + (\delta - w^{(i)}) F_{1/2}' + \frac{1}{2} (\delta - w^{(i)})^2 F_{1/2}'']. \quad (4.10)$$

Here $F_{1/2}'$ means $dF_{1/2}(\eta)/d\eta$ evaluated at $\eta = \eta_0$ and $F_{1/2}''$ means $d^2 F_{1/2}/d\eta^2$ evaluated at $\eta = \eta_0$. Bringing Σ through the square bracket gives

$$N = 2\pi^{-1/2} \cdot 4N_c [F_{1/2}(\eta_0) + (\delta - \bar{w}) F_{1/2}' + \frac{1}{2} (\delta^2 - 2\delta\bar{w} + \bar{w}^2) F_{1/2}'']. \quad (4.11)$$

Here

$$\bar{w} = \frac{1}{4} \Sigma w^{(i)}, \quad \bar{w}^2 = \frac{1}{4} \Sigma w^{(i)2}.$$

N as given by Eq. (4.11) must be equal to N in the unstrained state:

$$N = 2\pi^{-1/2} N_c \cdot 4F_{1/2}(\eta_0). \quad (4.12)$$

Eqs. (4.11) and (4.12) give for δ to terms of second order in the $w^{(i)}$

$$\delta = \bar{w} - \frac{1}{2} \frac{F_{1/2}''}{F_{1/2}'} (\bar{w}^2 - \bar{w}^2). \quad (4.13)$$

Expanding the free energy in a similar way gives

$$A_e = \Sigma A^{(i)} = 2\pi^{-1/2} N_c kT \cdot 4 [(\eta_0 + \delta) F_{1/2}(\eta_0) + \eta_0 (\delta - \bar{w}) F_{1/2}' + (\delta^2 - \delta\bar{w}) F_{1/2}'' + \frac{1}{2} \eta_0 (\delta^2 - 2\delta\bar{w} + \bar{w}^2) F_{1/2}''' - (2/3) F_{3/2}(\eta_0) - (2/3) (\delta - \bar{w}) F_{3/2}' - \frac{1}{3} (\delta^2 - 2\delta\bar{w} + \bar{w}^2) F_{3/2}'']. \quad (4.14)$$

Here primes have been introduced to denote derivatives in the way described in connection with Eq. (4.10).

Introducing Eq. (4.12) and Eq. (4.13) into Eq. (4.14) gives the energy in terms of the $w^{(i)}$:

$$A_e = NkT \left[\eta_0 - \frac{2}{3} \frac{F_{3/2}(\eta_0)}{F_{1/2}(\eta_0)} \right] + NkT \bar{w} + NkT (\bar{w}^2 - \bar{w}^2) \left[- \frac{F_{1/2}'}{2F_{1/2}(\eta_0)} \right]. \quad (4.15)$$

The first term here is the free energy of the electron gas when the crystal is unstrained. The second term is linear in the strain and gives rise to the dilatation described in the preceding section. The third term is quadratic in the strain and represents a change in the elastic constants. This change can be elucidated by comparing Eq. (4.15) with the elastic strain energy:

$$W_g = \frac{1}{2} \left[B(\epsilon_{11} + \epsilon_{22} + \epsilon_{33})^2 + \frac{4}{3} C'(\epsilon_{11}^2 + \epsilon_{22}^2 + \epsilon_{33}^2 - \epsilon_{11}\epsilon_{22} - \epsilon_{22}\epsilon_{33} - \epsilon_{11}\epsilon_{33}) + 4c_{44}(\epsilon_{23}^2 + \epsilon_{13}^2 + \epsilon_{12}^2) \right]. \quad (4.16)$$

Here the coordinates 1, 2, 3 are the fourfold axes of the crystal. B is the bulk modulus and C' is the shear constant $C' = (1/2)(c_{11} - c_{12})$. When $w^{(i)}$, defined by Eqs. (2.2) and (4.6) is written in terms of the strain components referred to the cubic crystal axes it has the form

$$w^{(i)} = \frac{1}{kT} \left[(\Xi_d + \frac{1}{3}\Xi_u)(\epsilon_{11} + \epsilon_{22} + \epsilon_{33}) + \frac{2}{3}\Xi_u(\pm\epsilon_{23} \pm \epsilon_{13} \pm \epsilon_{12}) \right]. \quad (4.17)$$

In Eq. (4.17) the sign of $\epsilon_{\mu\nu}$ is the same as that of $a_{\mu}^{(i)}a_{\nu}^{(i)}$. It is easily shown by using Eq. (4.17) that

$$\overline{w^2} - \bar{w}^2 = \frac{4}{9} \frac{\Xi_u^2}{(kT)^2} (\epsilon_{23}^2 + \epsilon_{13}^2 + \epsilon_{12}^2).$$

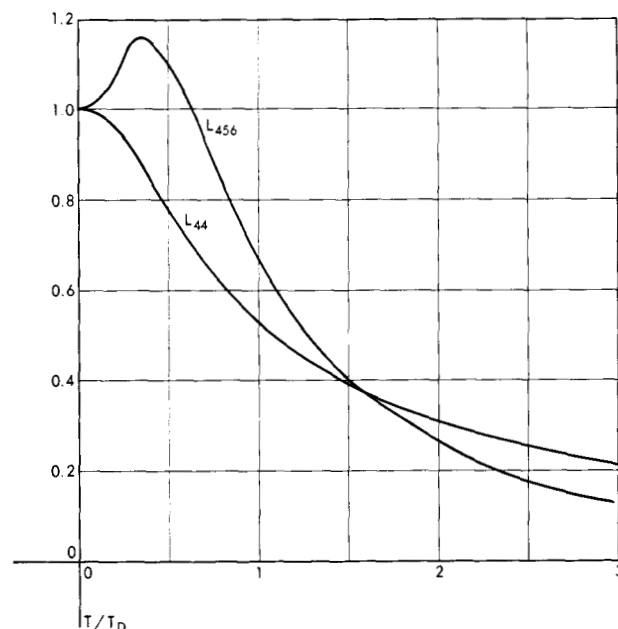
Substituting this into Eq. (4.15) and comparing with Eq. (4.16) shows that the only elastic constant affected by the electronic energy is c_{44} . The change of c_{44} is

$$\frac{\delta c_{44}}{c_{44}} = - \frac{N\Xi_u^2}{9c_{44}kT} \left[\frac{F_{1/2}'}{F_{1/2}(\eta_0)} \right]. \quad (4.18)$$

In Eq. (4.18) η_0 is to be determined from Eq. (4.12) at temperature T .

The temperature dependence of $(\delta c_{44}/c_{44})$ is conveniently referred to the degeneracy temperature T_D ,

Figure 1 The functions $L_{44}(\eta_0)$, Eq. (4.20), and $L_{456}(\eta_0)$, Eq. (4.26), which describe the temperature dependence of the electronic contribution to the elastic constants.



defined by the statement that the Fermi level approaches kT_D as T approaches zero. T_D is related to N by

$$T_D = \left(\frac{3}{32\pi} \right)^{2/3} \frac{h^2 N^{2/3}}{2m^*k}.$$

η_0 can be regarded as a parameter which determines T by

$$T = T_D (3F_{1/2}(\eta_0)/2)^{-2/3} \quad (4.19)$$

and $\delta c_{44}/c_{44}$ by

$$(\delta c_{44}/c_{44}) = (\delta c_{44}/c_{44})_0 L_{44}(\eta_0) \quad (4.20)$$

$$L_{44}(\eta_0) = (2/3) (3F_{1/2}(\eta_0)/2)^{2/3} (F_{1/2}'/F_{1/2}(\eta_0)).$$

$$\left(\frac{\delta c_{44}}{c_{44}} \right)_0 = - \frac{4}{3} \left(\frac{4\pi}{3} \right)^{2/3} \frac{m^* \Xi_u^2 N^{1/3}}{h^2 c_{44}}. \quad (4.21)$$

$L_{44}(\eta_0)$ approaches unity as $T \rightarrow 0$. At high temperatures $\delta c_{44}/c_{44}$ approaches the nondegenerate limit:

$$\frac{\delta c_{44}}{c_{44}} = \frac{N\Xi_u^2}{9c_{44}kT}. \quad (4.22)$$

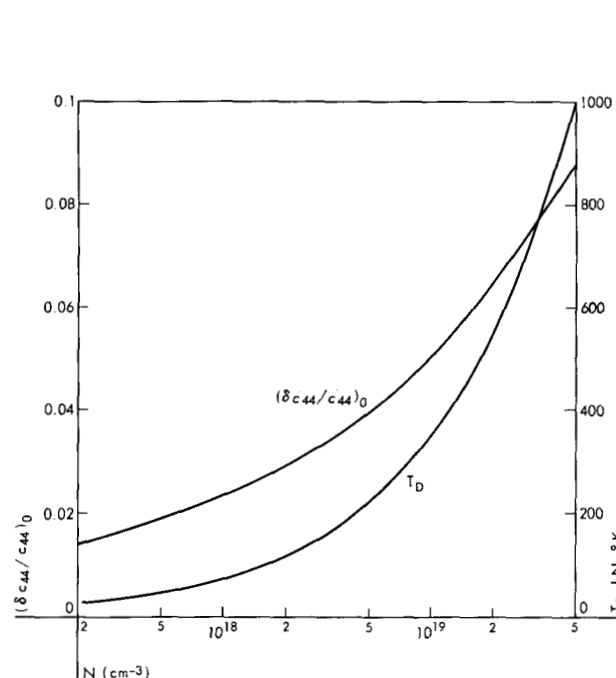
The temperature dependence of $(\delta c_{44}/c_{44})$ is plotted in Fig. 1. Numerical values for germanium are

$$(\delta c_{44}/c_{44})_0 = -2.1 \times 10^{-8} N^{1/3}$$

$$T_D = 7.3 \times 10^{-11} N^{2/3},$$

where N is in cm^{-3} and T_D is in $^\circ\text{K}$. These values are plotted in Fig. 2.

Figure 2 Values of T_D and $(\delta c_{44}/c_{44})_0$ for germanium.



The results obtained by retaining the terms of third order in the strain in the expansions of Eqs. (4.11), (4.14) and (4.15) are also presented here. The essential result is a value for the electronic contribution to the third-order elastic constants. The interest in this problem stems from the fact that the third-order elastic constants of pure germanium have recently been measured by Bateman, Mason and McSkimin.⁵

The retention of terms of third order in the strain in the earlier expansions of this section gives rise to an additional term in the equation for the electronic free energy, Eq. (4.15), of magnitude

$$A_e = NkT(\bar{w}^3 + 2\bar{w}^3 - 3\bar{w}\bar{w}^2) [F_{1/2}''/6F_{1/2}(\eta_0)]. \quad (4.23)$$

Here

$$\bar{w}^3 = \frac{1}{4} \sum w^{(i)3}.$$

When $w^{(i)}$ is expressed in terms of the strain components referred to the cubic crystal axes it is found that

$$\bar{w}^3 + 2\bar{w}^3 - 3\bar{w}\bar{w}^2 = \frac{16}{9} \left(\frac{\Xi_u}{kT} \right)^3 \epsilon_{23}\epsilon_{31}\epsilon_{12}. \quad (4.24)$$

A comparison of Eqs. (4.23) and (4.24) with the phenomenological definition of the third-order elastic constants^{5, 6} shows that they represent a contribution to c_{456} . The electronic contribution to c_{456} is

$$\delta c_{456} = \frac{4}{27} \frac{N\Xi_u^3}{(kT)^2} \left[\frac{F_{1/2}''}{F_{1/2}(\eta_0)} \right]. \quad (4.25)$$

When the temperature dependence of c_{456} is referred to the degeneracy temperature as described in connection with Eqs. (4.19) to (4.21), it can be written in the form

$$\delta c_{456} = (\delta c_{456})_0 L_{456}(\eta_0)$$

$$L_{456}(\eta_0) = (4/3) (3F_{1/2}(\eta_0)/2)^{4/3} (F_{1/2}''/F_{1/2}(\eta_0)) \quad (4.26)$$

$$(\delta c_{456})_0 = 2^{26/3} \pi^{4/3} 3^{-10/3} m^{*2} \Xi_u^3 / h^4 N^{1/3}. \quad (4.27)$$

The temperature-dependent function $L_{456}(\eta_0)$ is plotted in Fig. 1. The calculated values of δc_{456} at 77°K and 300°K are shown as functions of electron concentration in Fig. 3. Similar curves for other temperatures can easily be constructed with the aid of Eqs. (4.26) and (4.27) and Fig. 1.

The most interesting feature of δc_{456} is its large magnitude. Bateman, et al.,⁵ found that $c_{456} = -1.65 \times 10^{12}$ dyne/cm² for pure germanium. Thus, as can be seen from Fig. 3, the electronic contribution to c_{456} can be much larger than c_{456} of pure germanium. It appears that the measurement of the third-order elastic constants, although considerably less accurate than that of second-order constants, may provide a more sensitive test for electronic effects.

The high sensitivity of the third-order elastic constants to the electronic contribution is a result of the fact that in the electronic theory the strain is multiplied by a factor (Ξ_u/ζ) . Therefore, as the order of a term in the strain components increases, it contains an increasing number

of powers of the factor (Ξ_u/ζ) . Since deformation potential constants are usually in the range 1 to 10 ev, the result that third-order elastic constants have a high sensitivity to electronic contributions should be generally applicable to systems with an electronic degeneracy temperature of less than, say, 1000°K.

5. Model of the valence band

The structure of the valence band is much more complicated than that of the conduction band. Several simplifying approximations will be introduced here in order to obtain a tractable problem. As a consequence the results obtained must be regarded as suggestive rather than quantitative.

The model used is as follows:

(1) The valence band is regarded as an isotropic parabolic band. In other words, the hole energy as a function of crystal momentum is assumed to have the form $E = p^2/2m_v^*$. In particular, the effect of the valence band which is split off by spin-orbit coupling is neglected. This is a rather crude approximation, as doping levels at which the Fermi energy is larger than the spin-orbit splitting of the bands can be attained in germanium.

(2) Only the "heavy hole" band will be considered. This is because most of the holes are in the large mass band.

(3) The effect of strain on the band will be treated in the approximation introduced by Brooks,⁷ according to which the effect of strain on the energy of the state of crystal momentum $\mathbf{p}$ is

$$\delta E(\mathbf{p}) = \left[\Xi_u' \mathbf{1} + \Xi_s' \left(\frac{\mathbf{p}\mathbf{p}}{p^2} - \frac{1}{3} \mathbf{1} \right) \right] : \boldsymbol{\epsilon}. \quad (5.1)$$

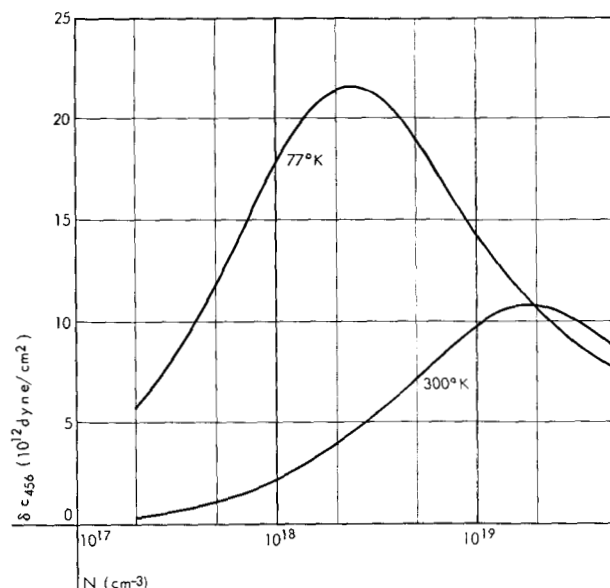


Figure 3 Values of the electronic contribution to c_{456} in degenerate germanium at 77°K and 300°K.

The parameters Ξ_s' and Ξ_d' are again known as deformation potential constants. Eq. (5.1) is only true for states sufficiently far from $\mathbf{p}=0$ that $E(\mathbf{p}) \gg \delta E(\mathbf{p})$. The fraction of states excluded by this condition is negligible in the present problem.

(4) The calculations will be carried out only for the strictly degenerate case, $\xi \gg kT$. A temperature dependence of the effect will appear when T approaches the degeneracy temperature.

6. Shear elastic constants of degenerate p-type Ge

As in the case of n -type germanium, the dilatational effect, described by Ξ_d' , leads to the change in volume previously discussed, but to no change in the elastic constants. It will not be considered further here. The effect on the shear constant will be investigated by calculating the energy of a pure axially symmetric shear strain:

$$\varepsilon = \varepsilon (\mathbf{e}\mathbf{e} - \frac{1}{3} \mathbf{1}). \quad (6.1)$$

With this strain the energy of state $\mathbf{p}$ is

$$E(\mathbf{p}) = (p^2/2m_v^*) + \Xi_s' \varepsilon (\cos^2 \theta - 1/3). \quad (6.2)$$

Here θ is the angle between $\mathbf{p}$ and the axis of strain, $\mathbf{e}$.

First it is necessary to calculate the Fermi level of the strained crystal. This is determined by the condition that the concentration of holes is N :

$$N = \int_0^\pi \int_0^\pi p(\zeta, \theta) (2/h^3) 2\pi p^2 dp \sin \theta d\theta. \quad (6.3)$$

From Eq. (6.2)

$$p(\zeta, \theta) = [2m_v^* \zeta - 2m_v^* \Xi_s' \varepsilon (\cos^2 \theta - 1/3)]^{1/2}. \quad (6.4)$$

When Eq. (6.3) is evaluated with the limit given by Eq. (6.4) it is found that

$$N = \frac{8\pi}{3h^3} (2m_v^* \zeta)^{3/2} \left[1 + \frac{1}{30} \left(\frac{\Xi_s' \varepsilon}{\zeta} \right)^2 \right] \quad (6.5)$$

to terms of second order in ε . The condition that N is independent of the strain shows that

$$\zeta = \zeta_0 \left[1 - \frac{1}{45} \left(\frac{\Xi_s' \varepsilon}{\zeta_0} \right)^2 \right], \quad (6.6)$$

where ζ_0 is the Fermi energy in the unstrained crystal.

The energy of the holes is

$$W_e = \int_0^\pi \int_0^\pi p(\zeta, \theta) (2/h^3) E(p) 2\pi p^2 dp \sin \theta d\theta. \quad (6.7)$$

By using Eqs. (6.4), (6.5) and (6.6), W_e is found to be

$$W_e = \frac{3}{5} N \zeta_0 - \frac{2}{15} \left(\frac{8\pi}{3} \right)^{2/3} m_v^* \Xi_s'^2 \varepsilon^2 N^{1/3}.$$

The elastic energy per unit volume of the strain defined by Eq. (6.1) is

$$W_g = \frac{2}{3} C \varepsilon^2,$$

where C is an elastic shear constant. (Because of the approximate nature of the calculation no attempt is made to distinguish between the two types of shear.) The change of C is therefore

$$\frac{\delta C}{C} = - \frac{1}{5} \left(\frac{8\pi}{3} \right)^{2/3} \frac{m_v^* \Xi_s'^2 N^{1/3}}{h^2 C}. \quad (6.8)$$

The resemblance of Eq. (6.8) to the corresponding equation for n -type germanium, Eq. (4.21) is apparent. Substituting values for p -type germanium from Table 1 Eq. (6.8) becomes

$$\frac{\delta C}{C} = -3.3 \times 10^{-10} N^{1/3}.$$

It is seen that this effect is two orders of magnitude smaller than the effect in n -type germanium. Two factors contribute to this result: (1) the numerical coefficient which appears in Eq. (6.8) is about one order of magnitude smaller than the coefficient in Eq. (4.21); (2) the deformation potential constant Ξ_s' is less than one-third Ξ_u . Thus, in spite of the facts that considerably larger values of N can be attained in p -type than in n -type germanium and that the theory presented is extremely crude, it appears that a much smaller effect is available for study in p -type germanium.

7. Effect of donors on the shear elastic constants of Ge

As explained in Section 1, electrons in germanium with fewer than 10^{17} donors per cm^3 are trapped in localized levels associated with the donor atoms at low temperatures. Experiments show that the energy of the bound electronic states is changed by elastic strain.⁸⁻¹¹ The theory of the change has been given by Price.^{12,13} The energy of occupied donor levels is part of the total energy of the semiconductor crystal. The change of the donor energy with strain is a contribution to the strain energy of the crystal. This dependence of the strain energy function of the crystal on the number of occupied donor levels implies a dependence of the elastic constants on donor concentration. The electronic contribution to the elastic constants of germanium containing donor impurities will be calculated in the following sections.

8. Model of the donor states

The reader is referred to papers published by several authors in 1955 and to the paper of Price for the full theory of the hydrogen-like donor states in germanium.¹²⁻¹⁶ Only a brief description of the content of these papers is given here.

In the effective mass approximation the hydrogenic $1s$ -like ground state of an electron bound to a donor has a degeneracy of four in an unstrained crystal. The four wave functions are the hydrogenic functions derived from the four valleys. Thus the Hamiltonian which determines the energy levels can be written

$$\mathcal{H} = \begin{vmatrix} -E_0 & 0 & 0 & 0 \\ 0 & -E_0 & 0 & 0 \\ 0 & 0 & -E_0 & 0 \\ 0 & 0 & 0 & -E_0 \end{vmatrix} \quad (8.1)$$

in a representation based on the individual single-valley hydrogenic wave functions. Here E_0 is the effective Rydberg in germanium and the zero of energy is the energy of the lowest state of the conduction band. Deviations from the effective mass approximation introduce additional elements $\mathcal{H}_{ij}$ into this Hamiltonian. Because of the equivalence of the valleys the most general way of introducing such elements modifies the Hamiltonian of Eq. (8.1) to the form

$$\mathcal{H} = \begin{vmatrix} -E_0 - \Lambda & -\Delta & -\Delta & -\Delta \\ -\Delta & -E_0 - \Lambda & -\Delta & -\Delta \\ -\Delta & -\Delta & -E_0 - \Lambda & -\Delta \\ -\Delta & -\Delta & -\Delta & -E_0 - \Lambda \end{vmatrix} \quad (8.2)$$

The energy levels determined by Eq. (8.2) are

$$\begin{aligned} E_1 &= -E_0 - \Lambda - 3\Delta \quad (\text{single}) \\ E_3 &= -E_0 - \Lambda + \Delta \quad (\text{triple}). \end{aligned} \quad (8.3)$$

Experiment shows that Λ and Δ are of the same order of magnitude. The quantity 4Δ is known as the chemical shift.

According to the theory of Price,¹² when the crystal is subjected to a homogeneous strain the Hamiltonian of Eq. (8.2) is to be modified by displacing each of the single-valley hydrogenic energies, the diagonal terms in Eq. (8.2), by the amount by which the strain displaces the energy of the valley from which the state is derived. In the following, for simplicity of notation we choose the zero of energy as $(E_0 + \Lambda)$ below the bottom of the conduction band, since the parameters E_0 and Λ do not enter into the theory of the effects of strain. Thus the Hamiltonian which determines the energy levels of a donor in a strained germanium crystal is

$$\mathcal{H} = \begin{vmatrix} E^{(1)} & -\Delta & -\Delta & -\Delta \\ -\Delta & E^{(2)} & -\Delta & -\Delta \\ -\Delta & -\Delta & E^{(3)} & -\Delta \\ -\Delta & -\Delta & -\Delta & E^{(4)} \end{vmatrix} \quad (8.4)$$

Here the $E^{(i)}$ are defined by Eqs. (2.2) and (2.3).

We shall also have occasion to refer to the form of the donor wave functions. The single-valley hydrogenic wave function of valley (i) has the form¹³

$$\psi^{(i)}(\mathbf{r}) = \phi^{(i)}(\mathbf{r}) u(\mathbf{k}^{(i)}, \mathbf{r}). \quad (8.5)$$

Here $u(\mathbf{k}^{(i)}, \mathbf{r})$ is the Bloch function at $\mathbf{k}^{(i)}$, the minimum point of valley (i) in $\mathbf{k}$ space, normalized in a unit cell. $\phi^{(i)}(\mathbf{r})$ is an envelope function which has the approximate form

$$\phi^{(i)}(\mathbf{r}) = (\pi b^2 a)^{-1/2} \exp\{-[(x^2 + y^2)/b^2 + z^2/a^2]^{1/2}\}. \quad (8.6)$$

The right-hand side of Eq. (8.6) is expressed in a

coordinate system in which the Z axis is the symmetry axis of the valley, one of the $[111]$ type axes. Since a and b are large compared to the lattice parameter of the crystal, $\phi^{(i)}(\mathbf{r})$ is a slowly varying function of position. It can be regarded as a constant over each unit cell for most purposes.

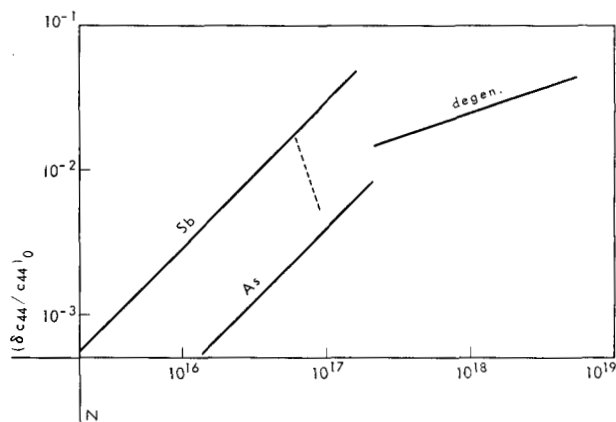


Figure 4 Calculated values for the electronic contribution to the elastic constant c_{44} of germanium at very low temperatures.

The lines in the left part of the Figure are calculated from the independent donor model, and refer to antimony and arsenic donors, respectively. The line in the right part of the Figure is calculated from the degenerate electron gas model, Sec. 4. The dotted line shows the estimate of the decrease in the effect due to interaction between donor states which is given in Sec. 10.

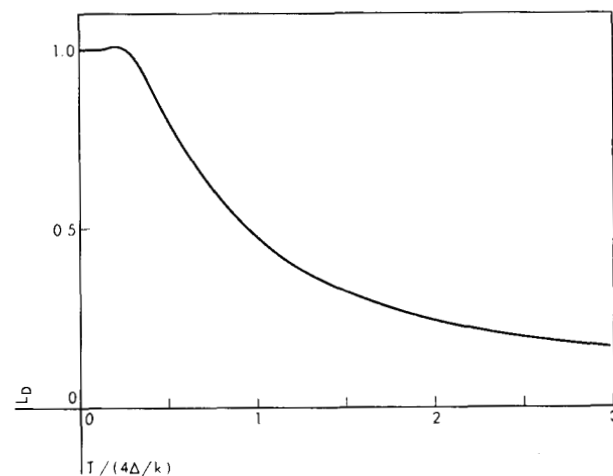


Figure 5 The temperature dependence of the electronic contribution to c_{44} due to excitation of electrons from the singlet ground state to the triplet.

The wave function of any bound donor state is a linear combination of the $\psi^{(i)}$ given by Eq. (8.5). The wave function of the lowest state in an unstrained crystal contains equal contribution from all of the valleys:

$$\psi(\mathbf{r}) = (1/2) \sum \psi^{(i)}(\mathbf{r}).$$

The coefficients of the $\psi^{(i)}$ in the donor wave functions of a strained crystal can be found from the Hamiltonian of Eq. (8.4).

The parameters of the donor states associated with the most important donor impurities are given in Table 2.

9. Calculation of c_{44}

The effect of the electronic energy on the elastic constants is determined by the solutions of Eq. (8.4) expanded to terms of second order in the $E^{(i)}$. This

Table 2 Properties of hydrogenic donor states in germanium

Property	Donor	Value
E_0		-0.0091 eV ^a
4Δ	P	3.0×10^{-3} eV ^b
4Δ	As	4.1×10^{-3} eV ^{b, c, d}
4Δ	Sb	5.6×10^{-4} eV ^d
b		64×10^{-8} cm ^a
a		23×10^{-8} cm ^a

^a See References 14, 15 and 16.

^b See Reference 10.

^c See Reference 9.

^d See Reference 8.

expansion can be worked out by first diagonalizing $\mathcal{H}$ with respect to Δ .

In one form this gives

$$\mathcal{H} = \frac{1}{4} \begin{pmatrix} -12\Delta + (E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)}) & (-E^{(1)} - E^{(2)} + E^{(3)} + E^{(4)}) \\ (-E^{(1)} - E^{(2)} + E^{(3)} + E^{(4)}) & 4\Delta + (E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)}) \\ (E^{(1)} - E^{(2)} + E^{(3)} - E^{(4)}) & (-E^{(1)} + E^{(2)} + E^{(3)} - E^{(4)}) \\ (E^{(1)} - E^{(2)} - E^{(3)} + E^{(4)}) & (-E^{(1)} + E^{(2)} - E^{(3)} + E^{(4)}) \end{pmatrix}$$

$$\begin{pmatrix} (E^{(1)} - E^{(2)} + E^{(3)} - E^{(4)}) & (E^{(1)} - E^{(2)} - E^{(3)} + E^{(4)}) \\ (-E^{(1)} + E^{(2)} + E^{(3)} - E^{(4)}) & (-E^{(1)} + E^{(2)} - E^{(3)} + E^{(4)}) \\ 4\Delta + (E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)}) & (E^{(1)} + E^{(2)} - E^{(3)} - E^{(4)}) \\ (E^{(1)} + E^{(2)} - E^{(3)} - E^{(4)}) & 4\Delta + (E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)}) \end{pmatrix}$$

Now the terms in the $E^{(i)}$ can easily be treated as a perturbation. The energy of the lowest state to terms of second order in the energy is

$$E = -3\Delta + (1/4) \sum E^{(i)} - (64\Delta)^{-1} [4 \sum E^{(i)2} - (\sum E^{(i)})^2]. \quad (9.1)$$

As before, $\sum$ means summation over the four valleys. We have previously used the result expressed by Eq. (9.1) in the theory of the scattering of phonons by donors in germanium.²² The similarity of Eq. (9.1) to Eq. (4.13) is evident and the evaluation of $(\bar{w}^2 - \bar{w}^2)$ given by Eq. (4.17) and the equation which follows it is also useful here. The total electronic energy in the low-temperature limit is N , the electron concentration, times the E given by Eq. (9.1). Thus it is seen, again by comparison with Eq. (4.16), that the change of c_{44} is

$$\left(\frac{\delta c_{44}}{c_{44}} \right)_{0D} = - \frac{N \bar{w}_u^2}{18 c_{44} \Delta} \quad (9.2)$$

and that the other elastic constants are not changed. (The subscript D is intended to indicate that the effect arises from donor impurity states.)

For antimony donors in germanium

$$(\delta c_{44}/c_{44})_{0D} = -N/3.5 \times 10^{18}. \quad (9.3)$$

This value and that for arsenic donors are plotted in

Fig. 3. Δ is larger for arsenic and phosphorus donors and the calculated value of $\delta c_{44}/c_{44}$ is correspondingly smaller. The values calculated for the degenerate case in Sec. 4 are also shown in Fig. 4 for comparison.

Eqs. (9.2) and (9.3) refer to the case in which all of the electrons are in the singlet state. Electrons will be excited out of this state at relatively low temperatures. In the case of antimony donors the triplet state is very close to the singlet, and excitation of electrons from the singlet into the triplet will destroy the effect in question at low temperatures. Other electronic states of the donor are much higher than the triplet, at least for antimony donors, and are ignored here.

The temperature dependence of $(\delta c_{44}/c_{44})_D$ due to excitation of electrons from the singlet to the triplet is most easily obtained by calculating the electronic free energy from the energy levels of a donor in a crystal subjected to a shear strain with a (111) axis. The energy levels for this case have been given by Price.¹² The details will not be given here. The result is that at finite temperature the value of $(\delta c_{44}/c_{44})_D$ given by Eq. (9.2) must be multiplied by the factor

$$L_D = [1 - e^{-4\Delta/kT} + (4\Delta/kT) e^{-4\Delta/kT}] / (1 + 3e^{-4\Delta/kT}). \quad (9.4)$$

This factor is plotted in Fig. 5.

10. Effect of donor interactions

The donors were considered as isolated non-interacting centers in the preceding section. In fact, however, the donor wave functions have a fairly large range, and at the concentrations at which the donor contribution to the elastic energy is measurable they overlap appreciably. The phenomenon of impurity conduction is a manifestation of this overlap of the donor wave functions.

The problem of the energy levels of a system of interacting donor states is extremely complicated. Progress is possible only when drastic simplifying approximations are introduced. One attempt to estimate the magnitude and type of effects to be expected is presented in the Appendix, in which the effect of strain on the energy of an electron bound to a pair of donor atoms is calculated. The calculations of the Appendix suggest that the interaction of donor states can have an important effect on the electronic strain-energy. Some generalization from the results for the two simple cases considered there is necessary for an evaluation of this effect. Such a generalization and evaluation is the objective of this section.

The strength of the interaction between donor states is measured by K , an exchange integral between electronic wave functions on different donor atoms. As discussed in the Appendix, there are two cases which can be treated simply: (1) the exchange integral has the value K for the wave functions derived from one valley and vanishes for the wave functions derived from the other three valleys; (2) the exchange integral has the value K for the wave functions derived from two of the valleys and vanishes for the wave functions derived from the other two valleys.

The electronic effect on the elastic constant is reduced by a factor of two when $K=4\Delta$ and by a factor 10 when $K=8\Delta$ in case (1), the case of interaction through one valley (see Fig. 7). On the other hand, in the case of interaction through two valleys the effect is almost unaffected by the interaction, its value for very large K being $4/3$ of its value for $K=0$. The difference between the two cases can be readily understood by considering Fig. 5. The effect becomes small in case (1) because the lowest state rapidly moves away from the other states when K increases. This has two consequences: (1) the energy denominators of the second-order perturbation all become large; (2) the matrix elements of the perturbation all become small because the ground state develops into a state derived from only one valley.

Case (2), two interacting valleys, is different because the energy difference between the lowest state and the next state remains small, approaching 2Δ at large K . The fact that no term in K is found in the lowest energy denominator here is a consequence of the assumption that $K^{(1)}$ is exactly equal to $K^{(2)}$. Such a phenomenon will not occur in general. In general the $K^{(i)}$ will all be different, will appear in all of the energy denominators to some degree, and will therefore reduce the electronic strain energy if they are much larger than Δ . In the

general case we expect that the energy levels will be rather haphazardly distributed through a region of width $2\bar{K}$ in energy, where $\bar{K}$ is some sort of average of the $K^{(i)}$.

When the interaction is large and of a general type some idea of the nature of the elastic phenomena can be obtained by treating Δ in the Hamiltonian of Eq. (A2) as a perturbation. We have not done this completely, but only to see the nature of the terms which occur. A typical quadratic term in the expansion of the energy in terms of the $E^{(i)}$ is

$$-\Delta^2(E^{(1)}-E^{(2)})^2/(K^{(1)}-K^{(2)})^3. \quad (10.1)$$

Now, it can be seen that the first terms of the factors L , Eq. (A8), and M , Eq. (A14), i.e., the terms $(1/\gamma^3)$ and $(1/\xi^3)$, are terms in the energy of just this form. They have the value one in the absence of interaction and the value $(4\Delta/K)^3$ in the case of large K . Thus they represent a change in the electronic contribution to the strain energy by a factor:

$$Q=64(\Delta/K)^3. \quad (10.2)$$

The comparison with Eq. (10.1) suggests that these first parts of L and M are typical of the general case and that the fact that the remaining parts of L and M have different form is a result of the special character of the interaction assumed in the derivation of Eqs. (A6) and (A12). Thus we conclude that the electronic strain energy should be modified by a factor given roughly by Eq. (10.2) in a theory of pairwise interaction of donors.

We use a simple scaled hydrogenic value

$$\bar{K}=(q^2/Kb)[1+(R/b)]\exp(-R/b) \quad (10.3)$$

for K in order to obtain numerical estimates. Here R is the distance between donors. It is related to the donor concentration by $(\pi/6)R^3=N^{-1}$. The Bohr radius has been replaced by b (see Eq. (8.6)) because the exchange integrals will receive their greatest contributions in cases in which the overlap of the wave functions is determined by b rather than by a .

The result of modifying the calculation of Sec. 9 by the present method is shown by the dotted lines in Fig. 3. When the interaction is small and Eqs. (10.2) and (10.3) give $Q>1$, $(\delta c_{44}/c_{44})_{0D}$ is calculated from Eq. (9.2). When $Q<1$ the result of Eq. (9.2) is multiplied by Q . The transition between formulas occurs at a donor concentration of about $6 \times 10^{16} \text{ cm}^{-3}$ for antimony donors. For arsenic donors Q is less than one up to the degeneracy concentration, $2 \times 10^{17} \text{ cm}^{-3}$. This very rough estimate of the effects of interaction of donors suggests that $(\delta c_{44}/c_{44})_{0D}$ will attain values greater than 1% in antimony-doped germanium and greater than 0.5% in arsenic-doped germanium.

11. Relation to experiment

Several experimental results which are relevant to the above calculations are available. The dilatational effect of gallium acceptors in germanium is definitely smaller

by at least a factor of two than that calculated¹⁷ in Sec. 3. The reason for this is not understood. It is possible, however, that the value used for Ξ_d' in Sec. 3 is in error by this amount.

Modern techniques for determining elastic constants usually depend on measurements of the velocity of elastic waves. It is therefore necessary to examine the effect of the temporal variation of the strain on the electronic strain energy. According to the theory presented in Secs. 3 and 4, the lowering of the energy of the strained crystal which accounts for the decrease of c_{44} depends on a re-establishment of statistical equilibrium of the electron populations of the valleys when the strain is applied. If the strain varies so rapidly that the electron populations cannot follow their equilibrium values, then the effect in question will not be present. The equilibrium of the electron populations is achieved by intervalley scattering. Hence, the condition for the existence of the effect in the presence of an oscillatory strain is that the frequency of the strain be small compared to the intervalley scattering rate. The total scattering rate in degenerate *n*-type germanium is about $2 \times 10^{13} \text{ sec}^{-1}$, which provides an upper limit to the intervalley scattering rate. A lower limit can be estimated to be 10^9 sec^{-1} in degenerate germanium.¹⁸

Thus it is seen that the elastic constants measured by the ordinary ultrasonic methods should include the effect of the electronic energy. In fact, the general features of the effect on c_{44} have recently been observed¹⁵ by measurements at 10 Mc/sec on germanium with a donor concentration of $3.5 \times 10^{19} \text{ cm}^{-3}$. However, the measured effect was only about three-fourths as great as the predicted one.

Another property which is sensitive to the elastic constants is the low-temperature specific heat. Bryant and Keeson have recently measured the Debye temperature of heavily doped *n*-type germanium.²⁰ It is not clear that the present calculation applies to the elastic waves which are important in this experiment, since phonons with frequencies up to $5 \times 10^{11} \text{ sec}^{-1}$ make significant contributions to the specific heat at 4°K. In any case, by using the tables of deLaunay²¹ and Eq. (4.21) it can be estimated that $(\delta\Theta_0/\Theta_0) = -6 \times 10^{-9} N^{1/3}$ for germanium. The effect found by Bryant and Keeson²⁰ has this sign and order of magnitude. The extent of quantitative agreement is difficult to evaluate because of the uncertainty of the

experimental result.

The interaction between elastic strain and donor electrons which is responsible for the change of c_{44} calculated here also is responsible for the scattering of phonons by occupied donors.^{22, 23} The rapid disappearance of this interaction when the antimony concentration is raised above $6 \times 10^{16} \text{ cm}^{-3}$ which is predicted by the theory of interaction of donor pairs should also be effective in eliminating the thermal resistance due to the donors. Goff and Pearlman²⁴ have measured the low-temperature thermal resistance of antimony-doped germanium over the concentration of range $5 \times 10^{15} \text{ cm}^{-3}$ to $2 \times 10^{18} \text{ cm}^{-3}$. They find that the thermal resistance varies smoothly and monotonically between the independent donor and the degenerate regimes, without evidence of the disappearance of the strain-electron interaction indicated by the dotted line of Fig. 3. This result suggests that our method of estimating the effect of the interaction of donor states is inadequate. It appears that although the effects of donor interaction are very important in the range $5 \times 10^{16} \text{ cm}^{-3}$ to $2 \times 10^{17} \text{ cm}^{-3}$, available theory does not furnish a satisfactory method of treating such effects.

Appendix: The effect of strain on the energy of an electron bound to a donor pair

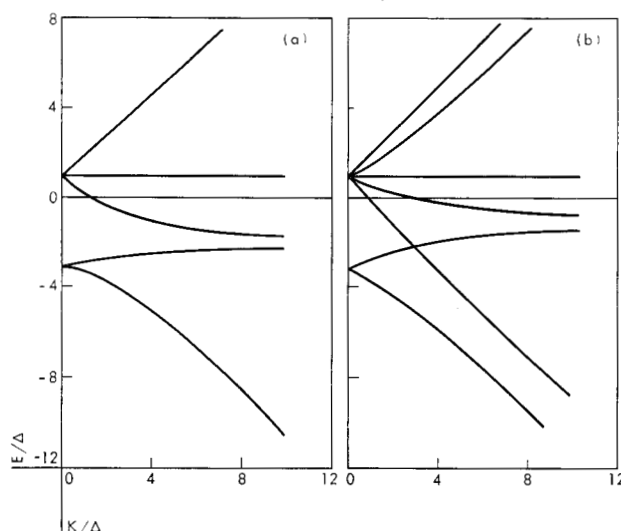
The problem of the energy levels of an electron bound to a pair of donor atoms is similar to that of the hydrogen molecule ion.²⁵ It is, however, much more complex because of the fact that the single donor hydrogenic wave functions are linear combinations of wave functions derived from the four valleys. The problem of the energy levels of two electrons bound to a pair of donor atoms is analogous to that of the hydrogen molecule.²⁶ This problem, is, however, related to that of the molecule-ion by the molecular orbital approximation, in which the energy of the molecule is regarded as the sum of contributions from one-electron states of the molecule-ion type.²⁷ Thus, in order to gain some insight, admittedly very rough, into the question of the effect of the interaction of donor states on the electronic contribution to the elastic constants, we will investigate the effect of strain on the energy levels of an electron bound to a pair of donors.

The Hamiltonian of an electron bound to a pair of donors has the form, by extension of Eq. (8.4):

$$\mathcal{H} = \begin{vmatrix} E^{(1)} + J^{(1)} & -\Delta & -\Delta & -\Delta & K^{(1)} & 0 & 0 & 0 \\ -\Delta & E^{(2)} - J^{(2)} & -\Delta & -\Delta & 0 & K^{(2)} & 0 & 0 \\ -\Delta & -\Delta & E^{(3)} + J^{(3)} & -\Delta & 0 & 0 & K^{(3)} & 0 \\ -\Delta & -\Delta & -\Delta & E^{(4)} + J^{(4)} & 0 & 0 & 0 & K^{(4)} \\ K^{(1)} & 0 & 0 & 0 & E^{(1)} + J^{(1)} & -\Delta & -\Delta & -\Delta \\ 0 & K^{(2)} & 0 & 0 & -\Delta & E^{(2)} + J^{(2)} & -\Delta & -\Delta \\ 0 & 0 & K^{(3)} & 0 & -\Delta & -\Delta & E^{(3)} - J^{(3)} & -\Delta \\ 0 & 0 & 0 & K^{(4)} & -\Delta & -\Delta & -\Delta & E^{(4)} + J^{(4)} \end{vmatrix} \quad (A1)$$

Figure 6 The energy levels of a pair of donor atoms.

(a) Overlap in only one valley, $K^{(1)}=K$, $K^{(2)}=K^{(3)}=K^{(4)}=0$. (b) Overlap in two valleys, $K^{(1)}=K^{(2)}=K$, $K^{(3)}=K^{(4)}=0$.

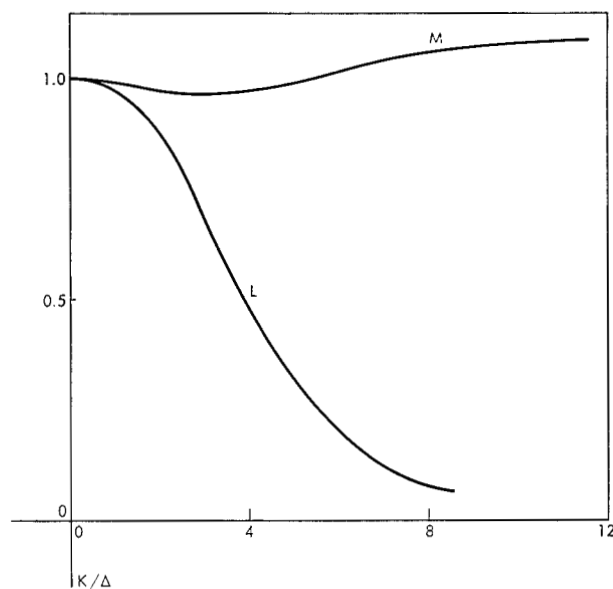


Here the first four states are the single-valley hydrogenic states of an electron on donor A and the second four states are the single-valley hydrogenic states of an electron on donor B . $K^{(i)}$ is the exchange integral of the wave functions of valley (i) , Eq. (42.12) of Reference 21. The $K^{(i)}$ will be different in general because of the differing anisotropies of the single-valley wave functions. The matrix elements of the type $\mathcal{H}^{(A i B j)} (i \neq j)$ are negligible because of the orthogonality of the wave functions of different valleys in the unit cell.²⁸ $J^{(i)}$ is the coulombic energy of an electron in the (i) wave function on donor A due to the presence of donor B , Eq. (42-8) of Reference 20. The orthogonality integral, Eq. (42-11) of Reference 14 has been neglected, since in the case of importance here the donors are separated by many effective Bohr radii. For the same reason the $J^{(i)}$ are essentially independent of (i) , and will be omitted below by shifting the zero of energy by an amount $J^{(i)}$. Then the Hamiltonian (A1) is easily diagonalized with respect to the $K^{(i)}$ to give

$$\mathcal{H} = \begin{vmatrix} E^{(1)} + K^{(1)} & -\Delta & -\Delta & -\Delta & 0 & 0 & 0 & 0 \\ -\Delta & E^{(2)} + K^{(2)} & -\Delta & -\Delta & 0 & 0 & 0 & 0 \\ -\Delta & -\Delta & E^{(3)} + K^{(3)} & -\Delta & 0 & 0 & 0 & 0 \\ -\Delta & -\Delta & -\Delta & E^{(4)} + K^{(4)} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & E^{(1)} - K^{(1)} & -\Delta & -\Delta & -\Delta \\ 0 & 0 & 0 & 0 & -\Delta & E^{(2)} - K^{(2)} & -\Delta & -\Delta \\ 0 & 0 & 0 & 0 & -\Delta & -\Delta & E^{(3)} - K^{(3)} & -\Delta \\ 0 & 0 & 0 & 0 & -\Delta & -\Delta & -\Delta & E^{(4)} - K^{(4)} \end{vmatrix} \quad (\text{A2})$$

Figure 7 The ratio of the effect of strain on the energy of a system of donor pairs to the effect of strain on the energy of isolated donors as a function of the exchange integral.

Curve L is given by Eq. (A8) and refers to exchange in only one valley. Curve M is given by Eq. (A14) and refers to exchange in two valleys.



Thus the $K^{(i)}$ appear in the Hamiltonian in the same way as the shifts of the valley energies with strain. However, the $K^{(i)}$ are not necessarily small compared to Δ , and cannot be treated by the perturbation theory used in deriving Eq. (9.1). In fact, the energy levels determined by (A2) cannot be found in the general case by simple algebraic methods.

In certain very special cases (A2) reduces to forms for which the energy levels have been given by Price.¹² These are (1) three of the $K^{(i)}$ have one value and the remaining $K^{(i)}$ has a different value; (2) two of the $K^{(i)}$ have one value and the other two have a different value. Case (1) is equivalent to that of a (111) axis of strain and case (2) is equivalent to that of a (110) axis of strain as considered by Price.¹²

To investigate case (1) let $K^{(1)}=K$ and $K^{(2)}=K^{(3)}=K^{(4)}=0$. Then the energy levels determined by the Hamiltonian of Eq. (A2) are¹²

$$E=\Delta \quad (\text{four}) \quad (\text{A3})$$

$$E=-\Delta(1\pm 2\gamma)\pm \frac{1}{2}K \quad (\text{A4})$$

where

$$\gamma=[1\pm (K/4\Delta)+(K/4\Delta)^2]^{1/2}. \quad (\text{A5})$$

Eqs. (A4) and (A5) determine four energy levels, since the sign of K and the sign of γ may be chosen independently. The sign of K must be the same in Eqs. (A4) and (A5). The energy levels are shown in Fig. 6a. (It should be remembered that the functions shown in Fig. 6 do not include the coulombic integral, J .) The dependence of the energy of the lowest state on strain is found by a procedure analogous to that leading to Eq. (9.1), namely, the Hamiltonian is diagonalized exactly with respect to K and Δ , and the effects of strain are included by perturbation theory. The result is

$$\begin{aligned} E &= -\Delta(1+2\gamma) - \frac{1}{2}K + \frac{1}{2}[E^{(1)} + \frac{1}{3}(E^{(2)} + E^{(3)} + E^{(4)})] \\ &\quad - \frac{1}{4\gamma} \left(1 + \frac{K}{2\Delta}\right) [E^{(1)} - \frac{1}{3}(E^{(2)} + E^{(3)} + E^{(4)})] \\ &\quad - \frac{3}{64\gamma^3\Delta} [E^{(1)} - \frac{1}{3}(E^{(2)} + E^{(3)} + E^{(4)})]^2 \\ &\quad - \frac{1}{36\gamma\Delta} \frac{1 - (K/2\Delta) + 2\gamma}{1 + (K/4\Delta) + \gamma} [E^{(2)2} + E^{(3)2} + E^{(4)2} \\ &\quad - E^{(3)}E^{(4)} - E^{(4)}E^{(2)} - E^{(2)}E^{(3)}] \end{aligned} \quad (\text{A6})$$

The valley which gives rise to the exchange integral will be randomly distributed among the four valleys of germanium in a doped crystal. Thus, to find the contribution of donor pairs to the strain energy function of the crystal we assume that the valley (1) of Eq. (A6) has a probability of one-fourth of being each of the four valleys. Summing over the four cases with $(N/4)$ electrons in each case we find for the quadratic term in the energy of the crystal

$$W_e(\text{quad}) = L \left(-\frac{N}{64\Delta} \right) [4\Sigma E^{(i)2} - (\Sigma E^{(i)})^2] \quad (\text{A7})$$

$$L = \frac{1}{3} \left[\frac{1}{\gamma^3} + \left(\frac{4}{3\gamma} \right) \left[\frac{1+2\gamma-K/2\Delta}{1+\gamma+K/4\Delta} \right] \right]. \quad (\text{A8})$$

It is apparent that the second part of Eq. (A7) is identical with the quadratic term in Eq. (9.1). Therefore the factor L , Eq. (A8), represents the change of the electronic contribution to the elastic constant due to the interaction of donors. The dependence of L on (K/Δ) is shown in Fig. 7.

To investigate case (2) above let $K^{(1)}=K^{(2)}=K$ and $K^{(3)}=K^{(4)}=0$. Then the energy levels determined by the Hamiltonian of Eq. (A2) are¹²

$$E=\Delta \quad (\text{two}) \quad (\text{A9})$$

$$E=\Delta \pm K \quad (\text{A10})$$

$$E=-\Delta(1\pm 2\xi)\pm K/2, \quad (\text{A11})$$

where $\xi \equiv [1 + (K/4\Delta)^2]^{1/2}$. Four levels are obtained from Eq. (A11) by choosing the signs of ξ and of K independently. The levels are shown in Fig. 6b.

We obtain for the energy of the lowest state in a strained crystal

$$\begin{aligned} E &= -\Delta(1+\xi) - K/2 + \frac{1}{4}(E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)}) \\ &\quad - \frac{K}{16\Delta\xi} (E^{(1)} + E^{(2)} - E^{(3)} - E^{(4)}) \\ &\quad - \frac{1}{64\Delta\xi^3} (E^{(1)} + E^{(2)} - E^{(3)} - E^{(4)})^2 \\ &\quad + \frac{1}{32\Delta} \frac{1 - \xi^{-1}(K/4\Delta)}{1 + \xi + (K/4\Delta)} (E^{(1)} - E^{(2)})^2 \\ &\quad + \frac{1}{32\Delta} \frac{1 + \xi^{-1}(K/4\Delta)}{1 + \xi - (K/4\Delta)} (E^{(3)} - E^{(4)})^2. \end{aligned} \quad (\text{A12})$$

As in case (1), the contribution of the electrons to the strain energy function involves averaging over all possible orientations of the valleys. Thus

$$W_e(\text{quad}) = M(-N/64\Delta) [4\Sigma E^{(i)2} - (\Sigma E^{(i)})^2] \quad (\text{A13})$$

$$M = \frac{1}{3} \left[\frac{1}{\xi^3} - \frac{2}{\xi} \left(1 + \frac{2(K/4\Delta)^2}{1+\xi} \right) \right]. \quad (\text{A14})$$

The factor M , which represents the change of the electronic contribution to the elastic constant because of the interaction of donors, has the values shown in Fig. 7.

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